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THE CRYSTAL STRUCTURE OF MONOADIPATO TETRAAQUO NICKEL (II)

THE title compound Ni $(C_6H_8O_4)$, $4H_2O$ was studied in this laboratory to investigate hydrogen bonding in crystalline solids as also to study the oxygen ligands around the metal.

Synthesis—The compound was prepared by the reaction of stoichiometric amounts of adipic acid and nickel carbonate and crystals were grown out of water solution. The crystals were thin elongated and platelike in appearance.

Crystal Data—Monoclinic with $a = 11{\cdot}70$, $b = 9{\cdot}77$, $c = 4{\cdot}75$ Å, $\beta = 99°\ 19'$, space group $P2_1/a$, $D_{obs} = 1{\cdot}70$ g/cc, $D_{cal} = 1{\cdot}71$ g/cc, $Z = 2$. Reflections (670) were collected using single crystal Weissenberg photography. The intensities were estimated visually and the data processed applying usual corrections. The relative intensities were brought to approximate absolute scale by statistical method.

Structure determination and comments—The structure is solved by the heavy atom technique. The metal atoms occupy special positions of centres of symmetry. The acid residues also occupy centres of symmetry. The water molecules are in general position.

A view of the crystal structure down [001] is shown in Fig. 1. In the crystal there is a six-fold co-ordination around nickel with distances ranging from 2·06 to 2·11 Å (shown by dotted lines). The structure is held together by ionic linkages and hydrogen bonds provided by the water molecules (shown by dashes and dots in the figure). The hydrogen bonds range from 2·65 to 2·96 Å. Chains of adipate anions are linked *via* water molecules parallel to [100].

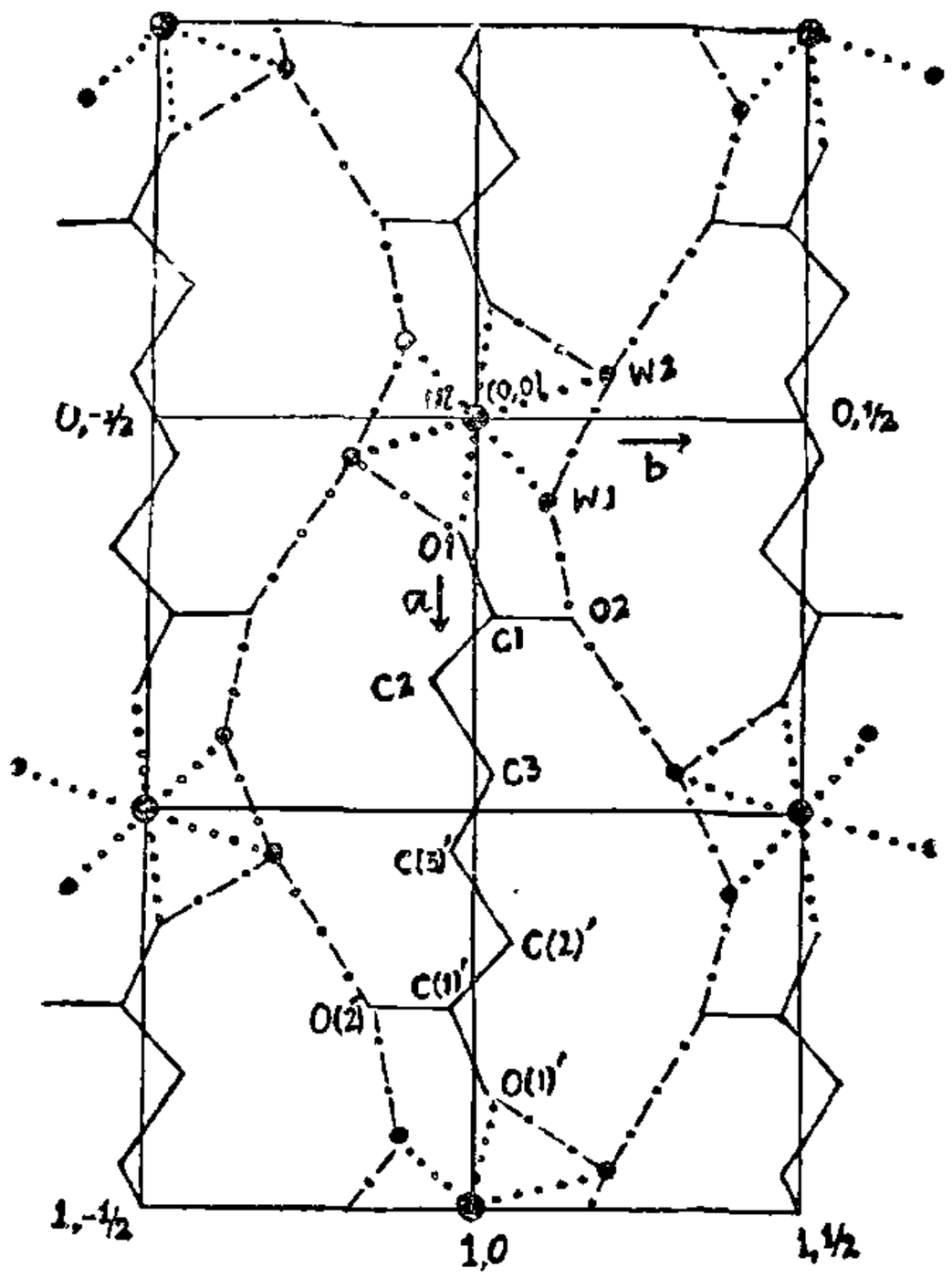

FIG. 1. The crystal structure down [001] axis.

Further work is in progress to locate the hydrogen atoms and to refine the positional and thermal parameters.

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FORMATION CONSTANTS AND THERMODYNAMIC PARAMETERS OF SOME POLY-HYDROXY PHENOLS

Experimental

ALL the chemicals used were of Analar quality. Polymetron model CL–41 pH-meter was used for pH-metric titrations. pH-metric titrations of free perchloric acid and perchloric acid with ligands, in aqueous medium, were carried out against standard caustic soda solution while maintaining the ionic strength at 0·1 M (sodium perchlorate).

Results and Discussion

The Irving-Rossotti method[1] was used for calculating $\bar{n}_A$ values and the protonation constants log $K_1^{H'}$ and log $K_2^{H'}$ by half-integral method. as suggested by

TABLE I

Ligand	Temp. °C	Linear plot method		Half integral method		Point-wise calculation		Average value	
		$\log K_1^H$	$\log K_2^H$	$\log K_1^H$	$\log K_2^H$	$\log K_1^{H'}$	$\log K_2^{H'}$	$\log K_1^H$	$\log K_2^H$
Resorcinol	30	9·75	8·57	9·75	8·57	9·83	8·52	9·78	8·55
	40	9·25	8·22	9·25	8·23	9·19	8·23	9·23	8·23
Catechol	30	10·23	8·72	10·10	8·70	10·21	8·60	10·18	8·67
	40	9·50	8·20	9·52	8·20	9·59	8·25	9·54	8·21
Hydroquinone	30	10·14	9·22	10·10	9·28	10·21	9·44	10·15	9·31
	40	9·68	8·93	9·69	8·80	9·65	9·01	9·67	8·91
Pyrogaliol	30	9·45	8·25	9·45	8·19	9·45	8·19	9·45	8·21
	40	9·00	7·85	9·00	7·88	9·11	7·88	9·03	7·87
Phloroglucinol	30	8·37	8·03	8·48	7·91	8·37	8·03	8·44	7·96
	40	8·18	7·52	8·18	7·49	8·00	7·54	8·12	7·52

Bjerrum[2]. Attempt has also been made to calculate these values using the following formulae:

$$p\,K_1^{H'} = pH + \log \frac{\bar{n}_A}{1 - \bar{n}_A}$$

and

$$p\,K_2^{H'} = pH + \log \frac{\bar{n}_A - 1}{2 - \bar{n}_A}\,.$$

The values so obtained are recorded in Table I under the heading point-wise calculation. Similarly $\log K_1^H$ and $\log K_2^H$ are obtained by plotting a graph between pH *vs.* $\log \bar{n}_A/1 - \bar{n}_A$ and pH *vs.* $\log \bar{n}_A - 1/2 - \bar{n}_A$ respectively (Figs. 2 and 3). The intercept on pH-axis has given the values for $\log K_1^H$ and $\log K_2^H$ which are also recorded in Table I under the heading linear plot method. The perusal of Table I shows that these values are in good agreement.

The values of protonation constants ($\log K_n^H$) were also obtained by half integral method making use of formation curves (Fig. 1). The values of pH at $\bar{n}_A = 0{\cdot}5$ and $\bar{n}_A = 1{\cdot}5$ give the values of $\log K_1^H$ and $\log K_2^H$ respectively. Figure 1 shows the formation curves and Figs. 2 and 3 linear plot at 30° C. Similar curves were obtained at 40° C. The results of $\log K_n^H$ are recorded in Table I.

The perusal of Table I shows the general order of protonation constants as follows:

Hydroquinone ≈ catechol > resorcinol > pyrogallol > phloroglucinol.

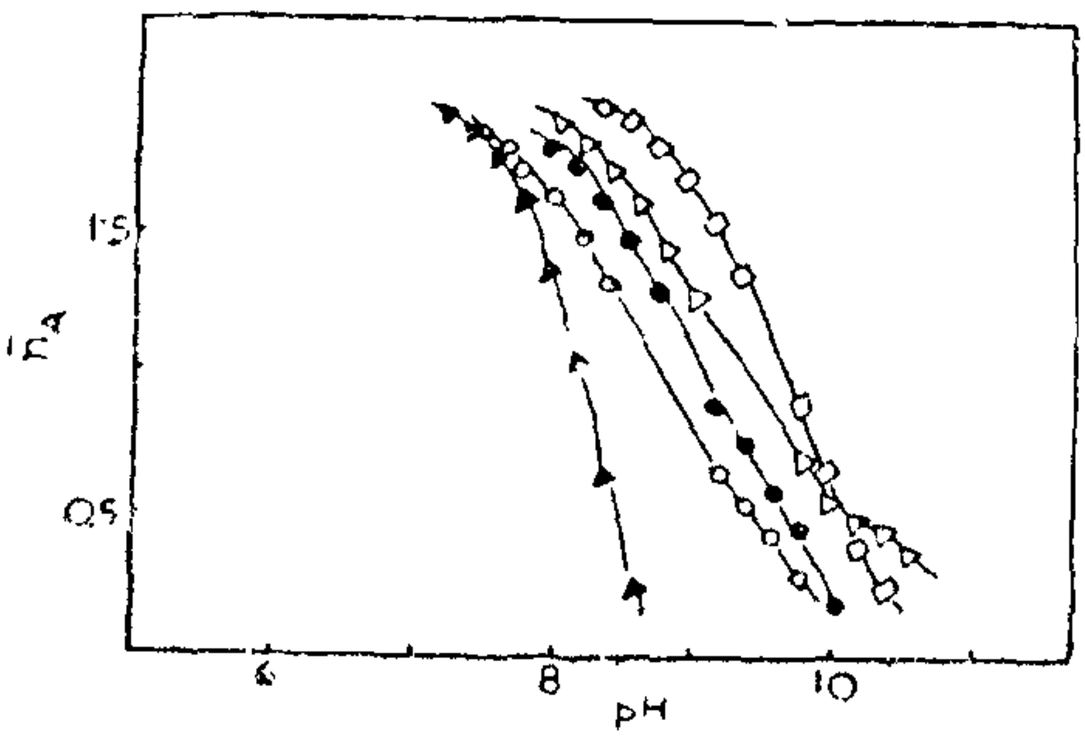

FIG. 1. Formation curves. ○—Pyrogallol; ▲—Phloroglucinol; ●—Resorcinol; △—Catechol; □—Hydroquinone.

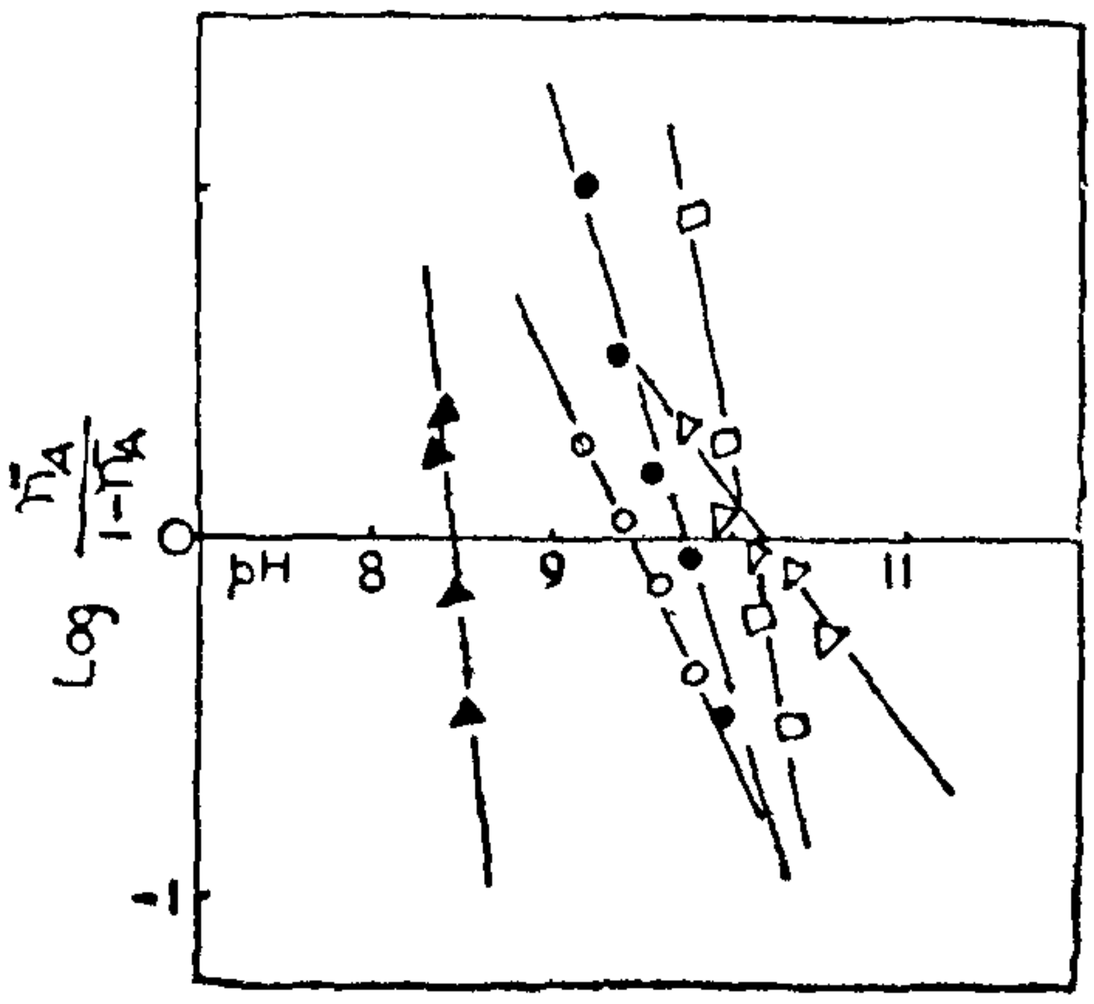

FIG. 2. Linear Plot Method for $\log K_1^H$. ○—Pyrogallol; ▲—Phloroglucinol; —Resorcinol; △—Catechol; □—Hydroquinone.

TABLE II

Temp. °C		Resorcinol	Hydroquinone	Pyrogallol	Phloroglucinol	Catechol
30	ΔF_1 Kcal. per mole	—13·64	—14·16	—13·18	—11·77	—14·20
	ΔF_2 Kcal. per mole	—11·93	—12·99	—11·46	—11·10	—12·10
40	ΔF_1 Kcal. per mole	—13·30	—13·93	—13·01	—11·83	—13·75
	ΔF_2 Kcal. per mole	—11·86	—12·84	—11·34	—10·83	—11·83
30	ΔS_1 e.u.	—31·12	—20·46	—14·13	—02·44	—52·74
	ΔS_2 e.u.	—45·87	—11·06	—15·25	—21·72	—24·36
40	ΔS_1 e.u.	—31·22	—20·54	—14·22	—0·217	—49·29
	ΔS_2 e.u.	—46·66	—11·19	—15·46	—21·89	—24·44
	ΔH_1 Kcal. per mole	—23·07	—20·36	—17·46	—12·51	—29·18
	ΔH_2 Kcal. per mole	—13·32	—16·34	—16·18	—17·68	—19·48

The values of free energy ΔF, enthalpy ΔH and entropy ΔS have been determined applying the standard equations[3]. The average values of ΔH, ΔS and ΔF are recorded in Table II.

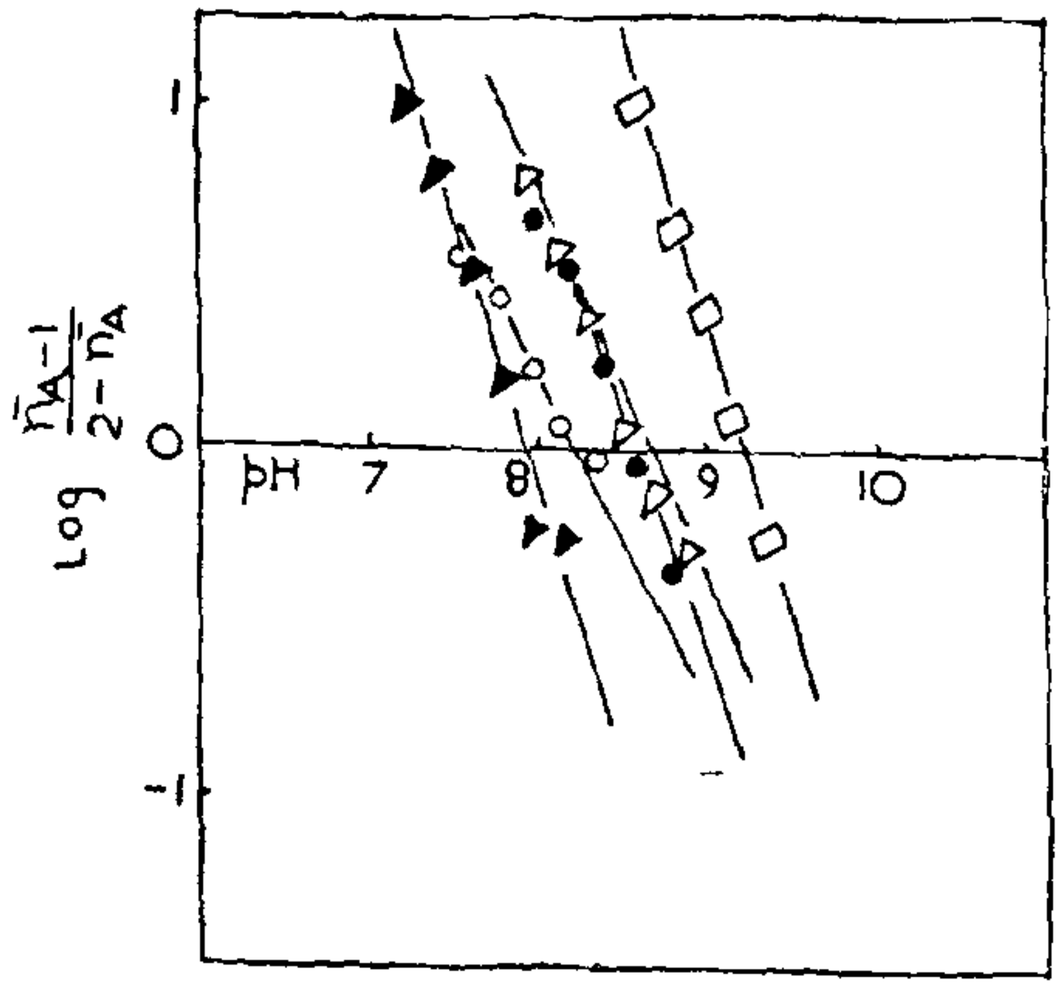

FIG. 3. Linear Plot Method for log K_2^H. ○—Pyrogallol; ▲—Phloroglucinol; ●—Resorcinol; △—Catechol; □—Hydroquinone.

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POLAROGRAPHIC STUDY OF PALLADIUM/ AMINO-ACID COMPLEXES

Introduction

THE electrochemistry of the halocomplexes of palladium[1,2], its ammine[3] and pyridine[4] complexes have been well investigated. The present paper deals with the study of the palladium complexes of three amino acids, namely glycine, valine and glutamic acid. The effects of pH, concentration of the ligand, reversibility, etc., have been examined critically. The number of electrons involved in the reduction of the complexes has been fixed by coulometry as 2·1 and the polarographic curves (though irreversible) have been found to be of analytical use in the pH range of 4·5–7 for estimating Pd upto 250 ppm.

Reagents

The ligand stock solutions of glycine, valine and glutamic acid were prepared in 0·1 M concentration from Analar chemicals. Other solutions were prepared by standard methods employing A.R. chemicals. Britton Robinson buffers[5] were employed for pH control. A pen recording polarograph (PO3) was used in this work. Capillary characteristics were $m = 2·71$ mg/sec., and $t = 3·74$ sec.

For the polarographic estimations, the final concentration of metal was about 10^{-4} M and the ligand concentration was always kept about 100 times that of metal to ensure complete complexation. The